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Near net-shape fabrication of hydroxyapatite glass composites

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Near net-shape fabrication of hydroxyapatite (HA) glass composites has been attempted by infiltrating a glass into porous HA performs. Main efforts were put to develop glasses that are chemically compatible with HA at elevated temperatures. After extensive investigations in the phosphate and borosilicate systems, glasses of (50-55)SiO_2-(20-25)B_2O_3-(10-20)Li_2O-(0-6)CaO (wt%) composition were successfully developed. The glass shows good chemical compatibility with HA at elevated temperatures. Dense HA/glass composites can be fabricated at 850–950 °C by the melt infiltration process. Investigations demonstrated a good near net-shape capability of the process, where the linear shrinkage induced by the infiltration process is less than 0.1%. Preliminary mechanical tests showed that the fracture strength and toughness of the infiltrated HA/glass composite are comparable with dense HA.

1. Introduction

Hydroxyapatite (HA) is one of the most attractive materials for biomedical implants applications, including maxillofacial, craniofacial, dental, intervertebral and orthopaedic implants [1, 2]. However, the fabrication of these implants is challenging not only because many of these applications require complex shapes and precise controls of dimensions, but also because post-machining for ceramics is a very difficult and quite expensive process [3, 4]. Near net-shape processing, aiming at an accurate dimensional control and minimization of the production cost, is therefore often considered as an alternative. The melt infiltration process, whereby a melt is infiltrated into a porous perform by the capillary force, is one of the cost-effective near net-shape processes, and has been applied to fabricate a number of engineering ceramic composites (e.g., reaction-bond SiC) [5, 6]. It has also been successfully commercialized to fabricate all-ceramic dental crowns with a satisfactory dimension control and good mechanical properties [7]. The fabrication of hydroxyapatite composites by the melt infiltration process will be also advantageous because the densification temperature for the composite can be significantly reduced and good net-shape capability could be achieved [8]. HA-polymer composites have already been fabricated by the process in literature [8, 9], but the fabrication of hydroxyapatite glass composites using the melt infiltration process has not yet been achieved up to now.

In fact, many types of glasses have already been used in conjunction with HA in the literature, either as sintering aids or as second phase reinforcements [10–16]. These studies generally showed that all these glasses promote the decomposition of HA into other calcium phosphates like tricalcium phosphates (TCPs). For example, the addition of 4 wt% 75P_2O_5-25Al_2O_3 (mol%) glass can result in 36–48 vol% TCP phases in the final composites depending on sintering temperature [13]. The decomposition of HA into TCP phases induces volume changes, which makes the reinforcement effects quite complex. A small amount of TCP phases in the composite may strengthen HA due to the partial stresses induced by the volume change, whereas a large quantity of TCP phases can seriously deteriorate mechanical properties of HA [10, 13, 14]. As a result, the mechanical properties of HA/glass composites reported in literature show a large scatter with the strength ranging from 8 to 206 MPa [10–15], where the highest fracture strength was reported by Kondo *et al.* [10] in 1984. Kangasniemi *et al.* [16] has tried to incorporate

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a large quantity of SiO_2-CaO-P_2O_5-Na_2O glasses in HA (e.g., 1:1 or 7:3 in glass to HA weight ratio). They found that these glasses are very reactive to HA, where after sintering at 700–1300 °C for 1 h, HA was totally converted to β-rhenanite and wollastonite. Obviously, the glasses employed in the literature are too reactive to HA and are not suitable for the infiltration to HA. Therefore, a glass that is chemically compatible with HA at elevated temperatures needs to be developed first before the infiltration process can be applied to manufacture HA glass composites.

The primary goal of the present study is to achieve near net-shape fabrication of HA glass composites by the melt infiltration process. Efforts were put to develop HA-compatible glasses as well as to characterize net-shape capability of the melt infiltration process.

2. Experimental

2.1. Glass development

Glasses were explored in various systems. Three criteria were adopted for screening glasses. Namely: (1) The glass should be chemically compatible with HA at elevated temperatures; (2) The glass should have a low viscosity at 900–1000 °C; (3) The glass should have a good leaching resistance. The general procedure for the glass development is illustrated in Fig. 1. The glass development starts from the composition design. To obtain a proper composition guess, one often needs to combine information from various sources like literature data, phase diagrams, the viscosity model [17], etc. If the guessed composition forms a glass after quenching in water at room temperature, two experiments are performed to verify the above three criteria. First, leaching tests are employed to check the leaching resistance of the glass. Second, infiltration tests are performed on HA below 1000 °C, from which the other two criteria can be verified, e.g., the check of the shape of a glass melt during infiltration and the infiltration distance after the infiltration process gives clear indications about whether the viscosity is sufficiently low; XRD and SEM investigations on infiltrated samples provide information on the chemical compatibility of a glass with HA at infiltration temperatures. If the above two experiments generate positive results, the infiltrated HA-glass composites are characterized by mechanical property measurements.

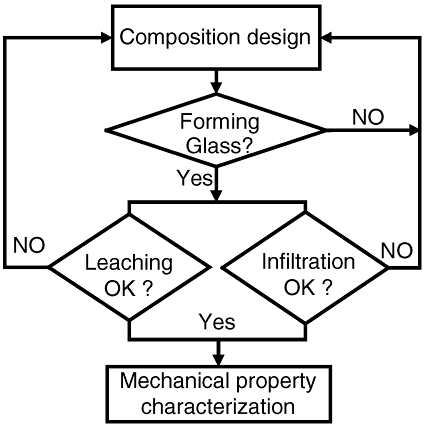

Figure 1 A schematic of the glass development procedure.

Glasses were melted on a 10–20 g scale. Borosilicate glasses are made through melting mixtures of oxides and carbonates in a Pt crucible at 1250–1400 °C in air for 2–4 h, followed by quenching glass melts in water. In the case of phosphate glasses, ammonium dihydrogen phosphate was first heated up to 450 °C for 5–7 h in an Al_2O_3 crucible to obtain P_2O_5. Other oxides or carbonates were then mixed with the resultant P_2O_5 in the Al_2O_3 crucible in proper proportions. The mixture was then heated to 1100–1300 °C for 2–4 h, followed by casting the glass melts on a copper plate at room temperature.

2.2. HA presintering and infiltration

A commercial HA powder (Merck, Darmstadt, Germany) was used to prepare porous HA performs. The powder was first sieved using a 0.25 mm mesh to get rid of large agglomerates, followed by uniaxially pressing under 5 MPa to form tablets of nominal dimensions of $60 \times 60 \times 6$ mm^3. The pressed tablets were then sintered at 1200 °C for 4 h in air. The sintered porous HA tablets served as preforms for infiltration. HA/glass composites were fabricated through infiltrating the sintered tablets with the glasses developed, e.g., by placing a piece of glass on the top of the tablet and heating the assembly to 850–950 °C for 1–4 h.

Tablets were also sintered at 1300 °C for 6 h to nearly full density under the mixed atmosphere of air and water vapor obtained by passing air through a water containing coil at room temperature. The dense HA was employed for the comparison of mechanical properties with infiltrated HA/glass composites.

2.3. Characterization

The shrinkage of samples before and after the glass infiltration was measured using a caliper with 10 μm resolution, from which the linear shrinkage was calculated.

The infiltrated samples were analyzed using X-ray diffractometry (XRD). The microstructure of infiltrated specimens was investigated using scanning electron microscopy (SEM).

The fracture strength was measured by a three-point bending test with a span of 10 mm and a crosshead speed of 0.5 mm/min in air using specimens with nominal dimensions of $3 \times 2 \times 15$ mm^3. Specimens for this test were cut from the infiltrated or sintered samples using a diamond saw, and ground using 80 grit SiC polishing papers. They were then lapped to the nominal dimensions using 320 grit SiC polishing papers. The fracture toughness was determined by the indentation strength (IS) method [18] on beams of the same dimensions as the strength test. Prior to fracture, an indentation was made by a Vickers indenter using a dwell time of 30 s under a load of 19.6 N. Special care was taken to orient one set of the radial cracks parallel to the cross section of the specimen where the prospective rupture would occur. Indented beams were fractured using the same fixture and procedure as the strength test. Every specimen was checked to confirm that the fracture was initiated from the indent. The fractured specimens that did not fail from the indention were excluded from the data pool of toughness evaluation. The fracture toughness was then calculated according to the equations in reference [18]. A total of 6–10 specimens were tested for both the strength and toughness tests.

2.4. Leaching resistance

The leaching resisance of various glasses was tested through immersing a piece of glass of ∼0.5 g into 50 ml distilled water at 70 °C for up to one week. The leaching rate (L) was then determined using the following equation.

$$L = \frac{W_0 - W_t}{W_0} \times 100 \times \frac{1}{t} \qquad (1)$$

where W_0 and W_t are the weight of a sample before and after the leaching test and t is the leaching time in minute. The leaching rate of a commercial glass (DURAN®, Schott Glass, Mainz, Germany) was also measured using the same procedure as above for comparison.

3. Results and discussion

3.1. Glass development

The glass development started from the phosphate glass system with the initial aim to achieve good leaching resistance together with low viscosity at ∼1000 °C. A group of phosphate glasses with relatively good leaching resistance were first tried. As illustrated in Fig. 2, the leaching rates for $60P_2O_5$-$25CaO$-$10B_2O_3$-$5Al_2O_3$, $55P_2O_5$-$29MgO$-$10B_2O_3$-$6Al_2O_3$, $57P_2O_5$-$26BaO$-$10B_2O_3$-$7Al_2O_3$ (mol%) are 6×10^{-6}, 5×10^{-5}, 2.2×10^{-5}%/min, respectively. In comparison, the leaching rate of the DURAN® glass was determined to be 1.8×10^{-5}%/min under the same conditions. However, the viscosity of these glasses is quite high even at 1100 °C and no infiltration could be achieved below 1000 °C. Attempts have also been made to reduce the viscosity of these glasses. It was found that partially replacing the alkali earth metal oxide in these glasses with Li_2O could significantly reduce the viscosity without sacrificing the leaching resistance too much. For example, 10 mol% Li_2O replacement of CaO from the $60P_2O_5$-$25CaO$-$10B_2O_3$-$5Al_2O_3$ glass can greatly reduce the viscosity while preserving good leaching resistance of the glass (Fig. 2). Infiltration investigations showed that HA preforms could be fully infiltrated by the glass within several minutes at 900 °C. However, the infiltrated composite contains almost no HA phases, as illustrated by the XRD pattern in Fig. 3, suggesting that severe reactions occurred between HA and the glass at the infiltration temperature. Actually, severe reactions were also found when HA preforms were infiltrated by the calcium, barium and magnesium phosphate glasses at 1200 °C. Several other types of phosphate glasses like $LiPO_3$ and $75P_2O_5$-$25CaO$, which exhibit low viscosities at 700–900 °C, were also investigated on their chemical compatibility with HA. These glasses are also quite reactive with HA. As exemplified in Fig. 3, HA almost completely decomposed into other calcium phosphates after the infiltration by these glasses. The present investigations combined with other investigations in literature [10–15] suggest that it is quite difficult to find a phosphate glass that could be chemically compatible with HA at elevated temperatures.

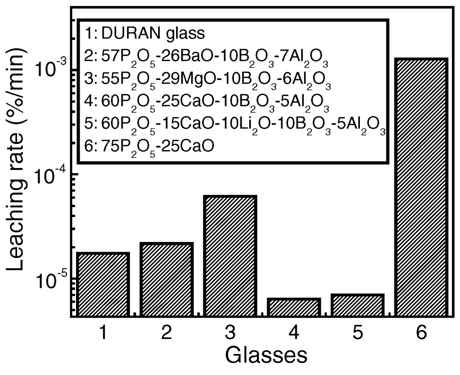

Figure 2 The leaching resistance of phosphate glasses.

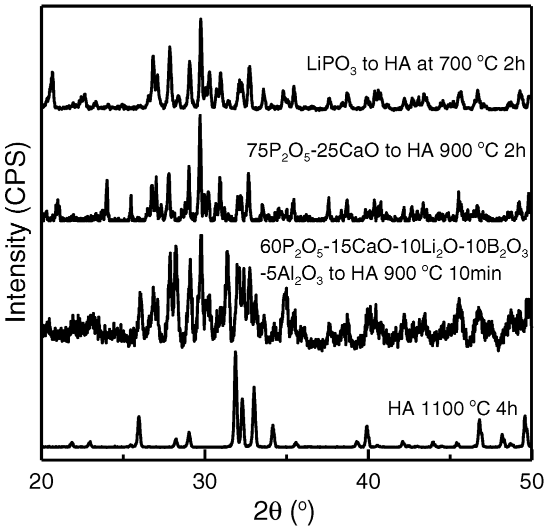

Figure 3 The XRD patterns of the infiltrated HA/phosphate glass composites.

The glass searching was continued on other systems with the main focus on the chemical compatibility of glasses with HA at high temperature. After extensively searching in various systems, glasses of (50-55)SiO_2-(20-25)B_2O_3-(10-20)Li_2O-(0-6)CaO (wt%) were successfully developed. These glasses are quite promising on several aspects. First, the glass is nearly chemically compatible with HA at least up to 1000 °C. After infiltration at 900 °C for 2 h, only a layer of reaction zone (∼1.5 mm) is observed between the remaining glass and the infiltrated dense region, and the dense part is only composed of HA and glass phases as confirmed by XRD investigations. The XRD pattern of the HA/glass composite infiltrated at 900 °C for 2 h is illustrated in Fig. 4, where all peaks fit quite well with those of HA (PDF No: 09-0432), although small amounts of other phases may also be present. Second, the glass has relatively good leaching resistance, where the leaching rate of the glass was determined to be 6×10^{-5} %/min in

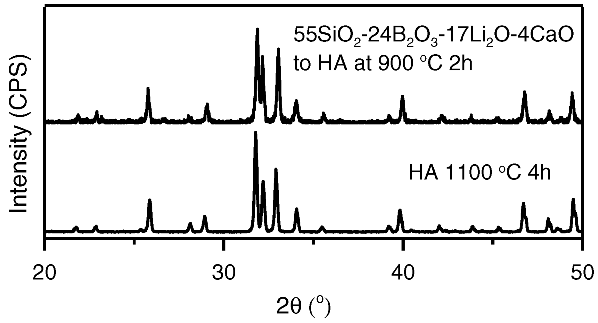

Figure 4 The XRD pattern of the infiltrated HA/borosilicate glass composite.

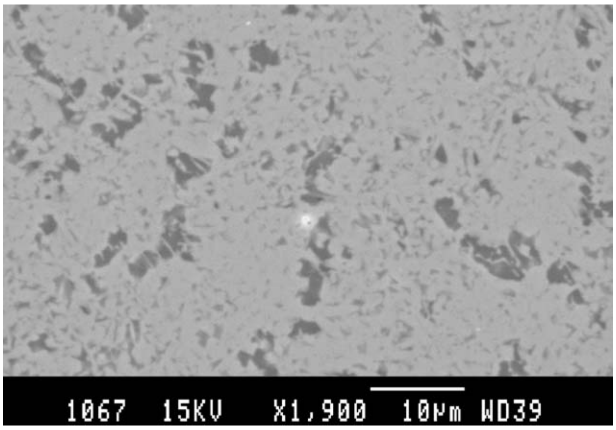

Figure 5 Typical microstructure of the infiltrated HA/borosilicate glass composite.

distilled water at 70 °C, which is just 3 times higher than that of the DURAN® glass. It should be noted that the leaching resistance of the glass might be further improved through adding small quantity of other oxides such as Al_2O_3. Third, the viscosity of the glass is quite low, where spontaneous infiltration is attainable at a temperature of 850 °C or higher. To our best knowledge, this is the most chemically compatible glass with HA at elevated temperatures.

3.2. HA glass composites

Dense HA glass composites can be fabricated through infiltrating the glass into presintered porous HA preforms at temperatures above 850 °C. This is the lowest temperature for fabricating dense HA/glass composites to date. Fig. 5 shows a typical microstructure of the infiltrated HA/glass composite, where the dark phases are glass and the grey phases are HA. The relative density of the infiltrated composite is estimated to be ∼92% of the theoretical density. Uninfiltrated pores up to 40 μm are frequently observed in the microstructure. These pores are mainly attributed to presintering-induced closed pores in the preform that cannot be reached by the molten glass during the infiltration process. Further increase in composite density is possible through optimizing the presintering and the infiltration process.

The dimensional changes during the infiltration process were characterized and compared with these of the sintering process. Within the measurement resolution of 10 μm, the physical dimensions of samples ($\sim 10 \times 10 \times 5$ mm^3) are identical before and after the infiltration by the glass at 900 °C, indicating that the linear shrinkage induced by the infiltration process is less than 0.1%. In comparison, sintering porous performs to nearly full density at 1300 °C induces linear shrinkage of 8.1%. These investigations demonstrated that the infiltration process has a quite good net-shape capability and is obviously much better than that of sintering process in terms of dimensional control.

Preliminary tests were performed to determine mechanical properties of the infiltrated HA/glass composites. The fracture strength and toughness of the composite are listed in Table I. The composite has a strength value of 76 MPa and a toughness value of 0.76 MPa·m$^{1/2}$, which are well in the ranges of the strength and toughness values, reported for HA composites in literature. It should be noted that the strength and fracture toughness data in the literature show quite a bit of scatter with strength values from 20–170 MPa [10, 13–15, 19–21] for the monolithic HA and 8–206 MPa [10–15] for HA/glass composites (glasses as the sintering aids), respectively. This scatter is mainly attributed to the differences in microstructure and phase constituents of the materials as well as the differences in testing procedures and atmospheres employed by different researchers. For a close comparison of the newly developed HA/glass composite with dense HA, HA was sintered to nearly full density and tested in the same procedure as the HA/glass composite, where a strength value of 76 MPa and a toughness value of 0.77 MPa·m$^{1/2}$ were obtained. Therefore, it can be concluded that the fracture strength and toughness of the newly developed HA/glass composite are comparable with those of dense HA. It should also be noted that the mechanical properties of the composite might be further improved if the fabrication process and the glasses were further optimized.

The present investigations demonstrate that near net-shape fabrication of HA glass composites can be achieved at a temperature much lower than ever reported in literature, while at the same time preserving mechanical properties of the composite comparable with those of HA. The lower processing temperature together with excellent net-shape capability should be

TABLE I Mechanical properties of dense HA and HA/glass composites

Materials	Linear shrinkage (%)	Fracture strength (MPa)	Fracture toughness (MPa·m$^{1/2}$)	Reference
HA/glass composites	<0.1	76 ± 14	0.76 ± 0.2	This study
Dense HA	8.1	76 ± 19	0.77 ± 0.1	This study
Dense HA	–	20–170	0.3–1.0	[10, 13–15, 19–21]

helpful for achieving accurate fitting and for reducing production cost for biomedical applications.

4. Conclusions

In order to fabricate HA glass composites through the melt infiltration process, glasses that are chemically compatible with HA at elevated temperatures were developed. Glasses in various systems have been investigated. It was found that phosphate glasses are quite reactive to HA at elevated temperatures and HA/phosphate glass composites cannot be obtained. After extensive search, glasses within the composition range of (50-55)SiO_2-(20-25)B_2O_3-(10-20)Li_2O-(0-6)CaO (wt%) were successfully developed. The glass is nearly chemically compatible with HA, has a relatively good leaching resistance and a low viscosity above 850 °C. Dense HA/glass composite could be fabricated by spontaneous infiltration above 850 °C. The linear shrinkage caused by the infiltration process is less than 0.1%, which is much lower than the shrinkage of 8.1% resulting from the sintering process. Mechanical tests showed that the fracture strength and toughness of the composite are 76 MPa and 0.76 $\text{MPa}\cdot\text{m}^{1/2}$, respectively, which are comparable with those of dense HA.

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